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# Microfluidic solvent extraction of platinum and palladium from a chloride leach solution using Alamine 336

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## **Abstract**

Microfluidic solvent extraction ( $\mu$ SX) of platinum and palladium from chloride leach solution using Alamine 336 had been conducted. The leach solution was produced by leaching of spent automotive catalysts. A microfluidic Y-Y channel embedded in a Pyrex™ microchip was used as the extraction system. Platinum and palladium extractions (> 99%) occurred at  $\mu$ SX contact time as fast as 1 sec with subsequent marginal extraction efficiency increases for longer contact times with comparable extraction performance to that of bulk SX. Findings from this preliminary study are useful in initiating a new metallurgical technique in the field of recovering precious (high-value) metals present in low concentrations which are otherwise not technically amenable (or economically viable) to extraction using current conventional methods.

**Keywords:** Microfluidics, solvent extraction, platinum-group metals, spent automotive catalyst

## **1. Introduction**

Microfluidics is scientific field that relates to the characteristics and manipulation of laminar fluid flows at very low Reynolds number (< 50) along micro-sized channels. The design of such systems affords benefits on numerous aspects such as enhanced surface area-to-volume ratio and faster diffusion which facilitate efficient liquid extractions and phase separations (Kim et al., 2000). Microfluidics systems are currently applied in the development of inkjet printheads, pharmaceutical industries and biomedical fields but its application in actual mineral processing

can be construed as unconventional although there were recent reports on such initiatives (Priest et al., 2011; Priest et al., 2012; Yin et al., 2012).

In conventional mineral processing industry, solvent extraction (SX) is used to separate and recover metal ions based on their relative solubilities in aqueous leach solution and organic extractant. Industrial-scale SX is generally conducted in a two-stage unit operation namely *mixing-settling* (Coulson et al., 1996). In the mixer stage, the two immiscible phases are dispersed in a turbulent regime to facilitate transfer of metal ions into the organic phase (extractant). The dispersion is then transferred to a settling tank where phase separation occurs. Recently, microfluidic SX ( $\mu$ SX) was proposed by Priest and co-workers (Priest et al., 2011; Priest et al., 2012) as a potential substitute to the mixing-settling SX process. It was suggested that  $\mu$ SX improved over the conventional bulk SX process as the former could bypass the settler stage and that undesirable particle-stabilized emulsions (crud) did not form in  $\mu$ SX (Priest *et al.*, 2011). In terms of a more mechanistic description, mineral  $\mu$ SX essentially functions by transmitting the aqueous leach solution and organic extractant in separate fine streams along two microchannels which merge into a single microchannel to bolster surface contact between the two immiscible streams. This increases the surface-to-volume ratio enabling enhanced metal ion transfer efficiency before the single microchannel reverts to its original two-microchannel configuration at the end of the extraction process.  $\mu$ SX has also been recently extended to two-phase solvent extraction of lanthanide ions as applied for used nuclear fuel processing (Nichols et al., 2011).  $\mu$ SX research is still in its infancy and more detailed studies are needed to further develop this technology, especially in regard to enhancing its efficiency for potential industrial-scale mineral applications.

In this study, extraction of platinum and palladium from a pregnant chloride leach solution (liquor) produced from a novel leaching method for spent automotive catalyst was conducted using the microfluidic approach. Such catalyst contains either platinum or platinum/palladium combinations which is used to transform carbon monoxide and hydrocarbons to carbon dioxide and moisture. Platinum group metals (PGM) are present in very marginal quantities in these catalysts (Benson et al., 2000; Jimenez de Aberasturi et al., 2011) but, given their high intrinsic value, it is worth recovering them provided an efficient extraction system can be developed. This essentially provides the main motivation for our current study.

## **2. Materials and methods**

### *2.1. Spent automotive catalyst leach solution*

The pregnant leach solution used in this project was generated by treatment of spent automotive catalysts using a patented process (Nicol and Nikoloski, 2011). The version of the process employed in this instance consisted of pre-treatment of the catalysts involving oxidative roasting in air at 500°C for 2 hours, followed by reductive roasting at the same temperature in a gas phase containing 5% H<sub>2</sub> + 95% N<sub>2</sub> for a further 2 hours. The dissolution of the platinum group metals from the pre-treated catalysts was achieved using a chloride leach solution containing 15% w/w HCl and 0.33% w/w AlCl<sub>3</sub>. The leaching was carried out at 25% solids for a period of 90 minutes in a baffled reactor maintained at a temperature of 90°C, with addition of a strong oxidizing agent. The primary leaching stage was followed by a solid/liquid separation and two stages of re-pulp washing of the residue, firstly in a solution containing 15% w/w HCl

and then in de-ionised water. Both washing stages were conducted in agitated vessels for periods of 60 and 30 minutes, respectively. The extractions achieved using this procedure were 99% for platinum and palladium and 90% for rhodium. Following partial recovery of these elements in a concentrated form, their concentrations were detected to be *ca* 19.4 (platinum), 10.8 (palladium) and 3.3 mg/L (rhodium) and this solution was then used as the aqueous phase in the current study of the microfluidic solvent extraction process.

## *2.2. Microfluidic setup and extraction*

A microfluidic Y-Y channel embedded in a Pyrex™ microchip (Institute of Microchemical Technology, Japan) was used for  $\mu$ SX. Two inlet channels (width = 100  $\mu$ m; depth = 40  $\mu$ m) merge at a Y-junction to form a single channel (width = 160  $\mu$ m; depth = 40  $\mu$ m; length = 120 mm – serpentine configuration) which separates into another identical Y-junction at the outlet (Fig. 1). Thermoplastic-based tubes were used to connect the two channel inlets (via Luer connectors) to two syringes, each containing the PGM leach solution and organic extractant. The organic extractant was produced using 5 vol. % Alamine 336 (Cognis) in kerosene. Alamine 336, a tertiary amine-based chemical ( $R_3N$ ), was selected as the organic extractant based on its effectiveness for extraction of platinum (Reddy et al., 2010). Liquid flow was executed using syringe pumps (NEW ERA Pump Systems, Inc., model: NE-300) and monitored using an optical microscope. The flowrates of the PGM leach solution ranged from 0.1 to 1.1 mL/hr and the organic/aqueous volumetric flow rate ( $R_f$ ) ratio was fixed at *ca* 0.65, since this ratio afforded the most stable microfluidic flow (Priest et al., 2011). Based on these flowrates, the  $\mu$ SX contact times ( $t$ ) of 1, 2, 4 and 7 sec were calculated in regard to the PGM leach solution and organic

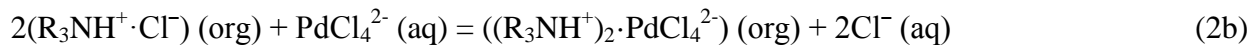
extractant contact duration along the main single channel. Bulk SX was conducted by agitating the PGM leach solution and organic extractant at the analogous organic/aqueous volume ratio of 0.65 in a plastic sample vial with contact time up to 20 seconds. The platinum, palladium and rhodium concentrations before and after the extraction processes were determined using inductively coupled plasma-mass spectrometry (Agilent 7500A ICP-MS).

### **3. Results and discussion**

#### *3.1. PGM solution and hydrometallurgical reactions*

The pH of the PGM leach solution was determined to be 1.72 using a pH meter equipped with Metrohm Unitrode electrode. From a purely *a priori* perspective, the low PGM concentrations (< 20 mg/L) render recovery using conventional bulk SX economically impractical since this necessitates usage of relatively bulkier mixer and settler systems. On the other hand, the comparatively ‘small’ equipment requirement of a microfluidic system may represent an opportunity to leverage on its ‘reduced plant footprint’ (Priest et al., 2012) with the possibility of good cost-effectiveness when applied to recovery of the abovementioned precious metals. It is acknowledged that the term ‘reduced plant footprint’ here can be construed as relative. However, the fact that the size of our  $\mu$ SX Pyrex™ microchip is merely 21 cm<sup>2</sup> indicates that the favorable small area requirement demonstrated here cannot be completely ignored.

The extraction process generally involves a two-step ion exchange reaction that results in formation of chlorocomplexes from Pt(IV) and Pd(II) (Rovira et al., 1998; Sanuki et al., 1999; Reddy et al., 2010):



In a typical Pt(IV) and Pd(II) recovery process, they are stripped from the organic complexes using either hydrolysis, anion exchange or reduction unit operations (Dhara et al., 1984). It should be noted, however, that the stripping process is excluded from this study.

### 3.2. Microfluidic solvent extraction

The single middle microchannel was separated into two by a guide structure which maintains the co-flow of the two liquids. Liquid flows were maintained for several minutes to ensure that the system has reached stability before samples were taken. In any case, it is essential to maintain continuous flow for both the aqueous and organic streams because flow discretization disrupts consistent ion diffusion across the liquid-liquid interface. The Reynolds numbers for all flows performed in this study are estimated to be lower than 5, indicating laminar flow with virtually non-existing mixing regime. This is an important feature of  $\mu$ SX



since it is desirable to ensure that ion diffusion is the dominant mass transfer mechanism at the phase interface. There was no observable significant blockage along the microfluidic channel during the extraction process as can be expected from solutions devoid of gangue particle. Similarly, the absence of crud formation may also be due to the absence of gangue. An added benefit in using microfluidic systems is attributed to the fact that these microchips are ‘closed’ systems as opposed to the more ‘open’ characteristic exhibited by conventional bulk SX. As such, there is likely to be reduced loss of volatile organics with significant implications for recycle rates and plant safety (Priest et al., 2012).

Fig. 2 shows the microfluidic extraction efficiencies with respect to contact time compared to bulk SX. Extraction data for rhodium are not shown because they are very marginal and do not appear to be amenable for extraction using Alamine 336. This observation coupled by the fact that the palladium extraction efficiencies are generally higher than platinum (except for  $t = 1$  sec) are essentially in good agreement with findings derived from Sun and co-researchers (2010 and 2011). This indicates the favorability of utilizing Alamine 336 to act as a selective extractor for palladium and/or platinum from PGM solutions. It is obvious that very significant palladium and platinum extractions ( $> 99\%$ ) occur at  $\mu$ SX contact time as fast as 1 sec with subsequent marginal extraction efficiency increases for longer contact times. Not surprisingly, palladium extraction undergoes 100% completion for  $t = 2, 4$  and 7 sec along with bulk SX which indicates very high affinity of Alamine 336 for palladium. It is clear that  $\mu$ SX exhibits comparable extraction performance to that of bulk SX and this has significant implication in terms of the former’s application as a precious metal recovery method from high-value/low volume aqueous streams. Understandably, it can be argued that  $\mu$ SX is a low-throughput technique, but this can be negated by its application for high-value/low volume streams such as

PGM solution. In fact, increase of  $\mu$ SX throughput can be accomplished via parallelization of microfluidic channels (i.e. stacked microfluidic chips or *numbering up*) (Schenk et al., 2003) and this could be the focus of future research.

#### **4. Conclusions**

A proof-of-concept for the preliminary application of  $\mu$ SX for extracting platinum and palladium ions from pregnant PGM chloride leach solution produced from a novel leaching method for spent automotive catalyst has been established. The comparable extraction efficiencies shown by  $\mu$ SX and its single-stage setup would justify further research in this area, particularly as a method to recover valuable metals from high-value/low volume streams.

#### **Acknowledgments**

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### Figure captions

**Fig. 1.** (a) Microfluidic Y-Y channel in serpentine configuration. (b) Schematic of the cross-section of the main (middle) channel.

**Fig. 2.** Extraction efficiency of the microfluidic system ( $\mu$ SX contact time = 1, 2, 4 and 7 sec) compared to bulk extraction.

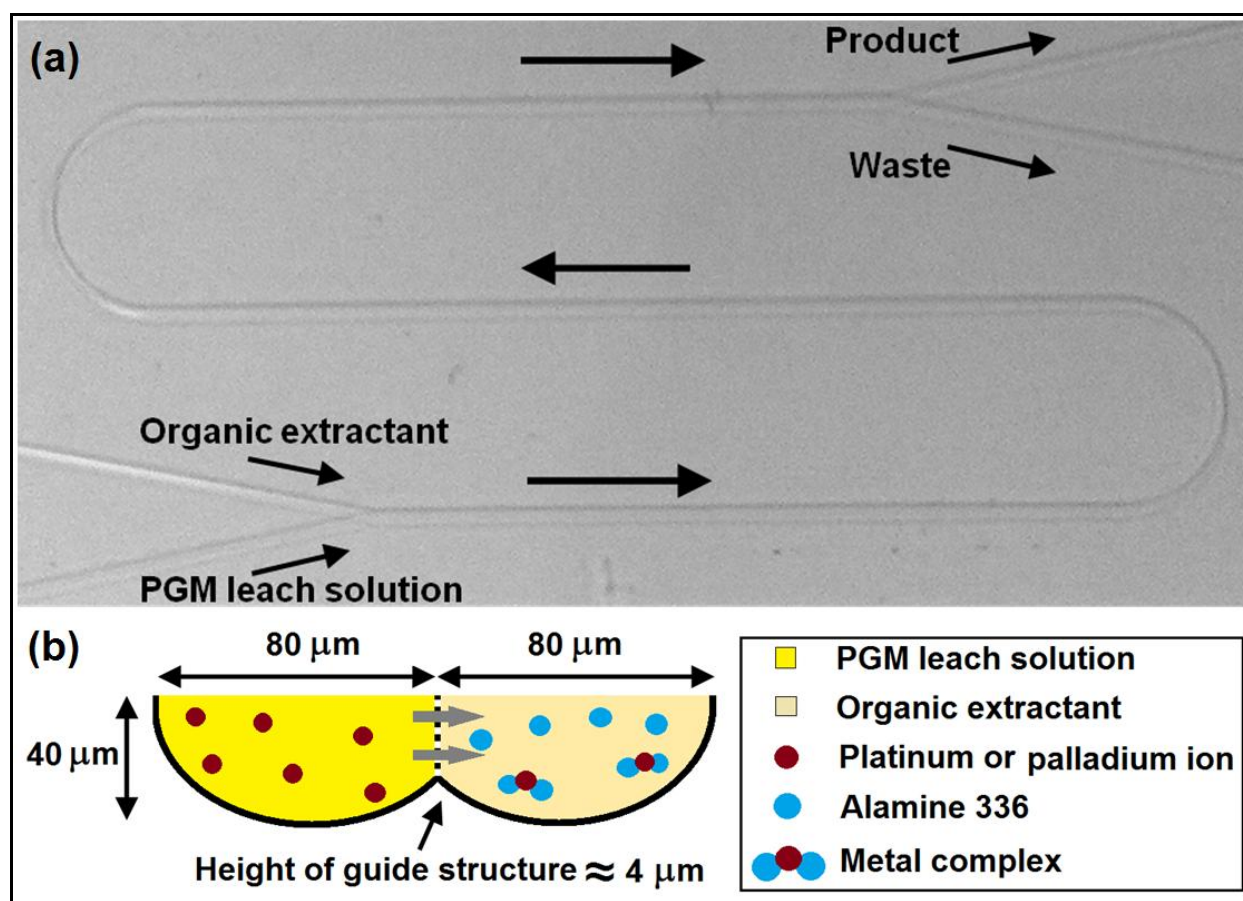


Fig. 1.

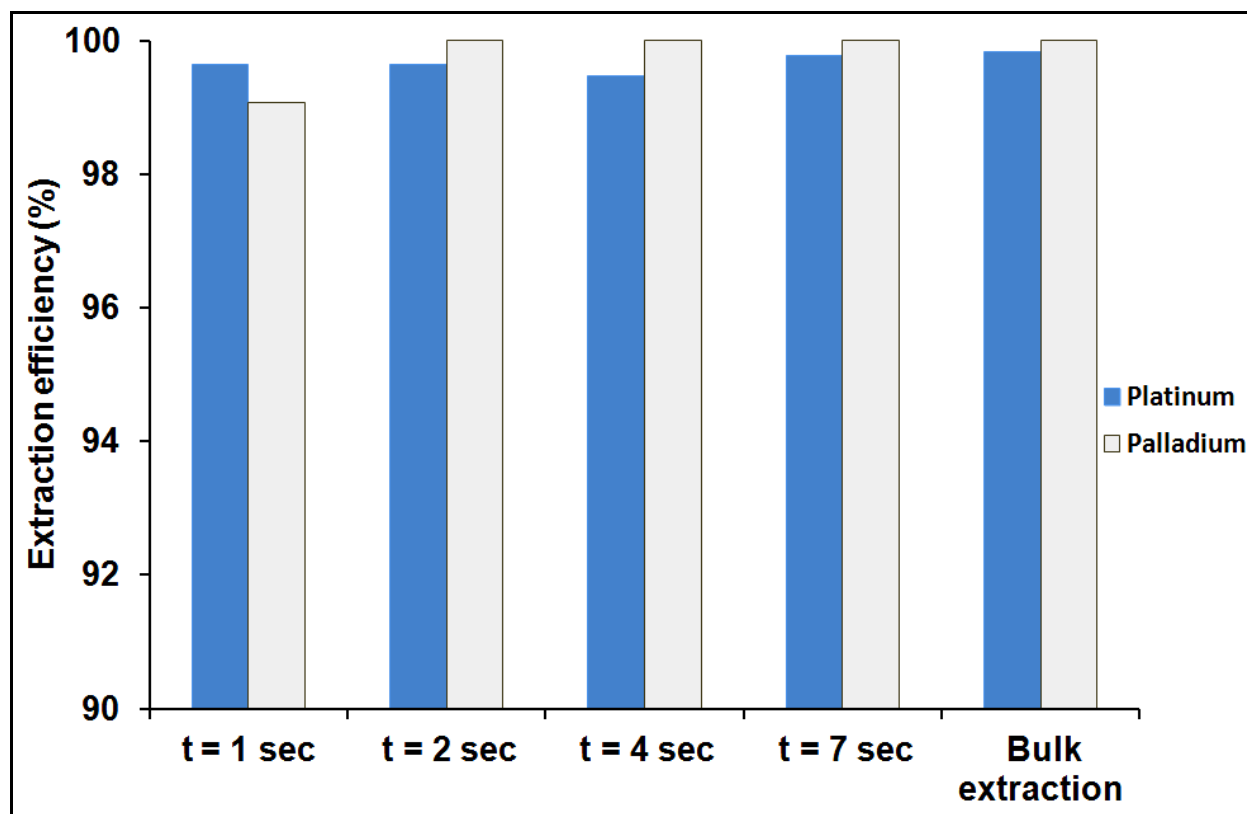


Fig. 2.